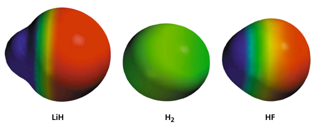
Chapter 1

Electronic Structure and Bonding

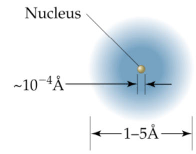
Acids and Bases



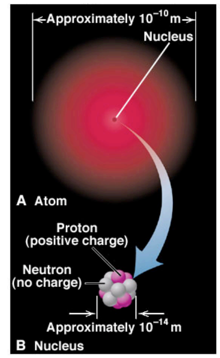
General Features of the Atom

Anders Jöns Ångström (1814-1874)

1 Å = 10 picometers = 0.1 nanometers = 10^{-4} microns = 10^{-8} centimeters



~ 0.1 nm



Nucleus = 1/10,000 of the atom

- *1 nm = 10 Å*
- *An atom vs. a nucleus ~10,000 x larger*

TABLE 1.2 The Ground-State Electronic Configurations of the Smallest Atoms

Atom	Name of element	Atomic number	1s	2s	$2p_x$	$2p_y$	$2p_z$	3s
H	Hydrogen	1	↑					
He	Helium	2	↑↓					
Li	Lithium	3	↑↓	↑				
Be	Beryllium	4	↑↓	↑↓				
B	Boron	5	↑↓	↑↓	↑			
C	Carbon	6	↑↓	↑↓	↑	↑		
N	Nitrogen	7	↑↓	↑↓	↑	↑	↑	
O	Oxygen	8	↑↓	↑↓	↑↓	↑	↑	
F	Fluorine	9	↑↓	↑↓	↑↓	↑↓	↑	
Ne	Neon	10	↑↓	↑↓	↑↓	↑↓	↑↓	
Na	Sodium	11	↑↓	↑↓	↑↓	↑↓	↑↓	↑

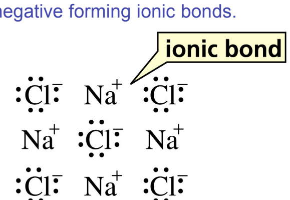
Electron Configurations

Noble Gases and The Rule of Eight

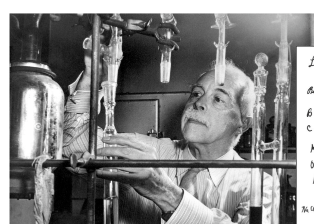
- When two nonmetals react to form a covalent bond: They share electrons to achieve a Noble gas electron configuration.
- When a nonmetal and a metal react to form an ionic compound: Valence electrons of the metal are lost and the nonmetal gains these electrons.

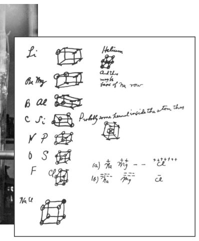
Ionic Compounds

- Ionic compounds are formed when electron(s) are transferred.
- Electrons go from less electronegative element to the more electronegative forming ionic bonds.



sodium chloride





G.N. Lewis

Photo Bancroft Library, University of California/LBNL Image Library

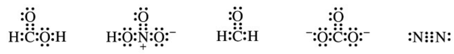
Footnote:
G.N. Lewis, despite his insight and contributions to chemistry, was never awarded the Nobel prize.

Notes from Lewis's notebook and his "Lewis" structure.

Covalent Compounds

- Share electrons.
- 1 pair = 1 bond.
- Octet rule (“duet” for hydrogen)
- Lewis structures:

Lewis structures



Notice the charges:
In one case they balance, can you name the compound?
In the other they do not, can you name the polyatomic ion?

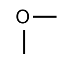
More about “formal” charge to come.

Important Bond Numbers

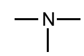
(Neutral Atoms!)

one bond H — F — Cl — Br — I —

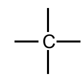
two bonds



three bonds



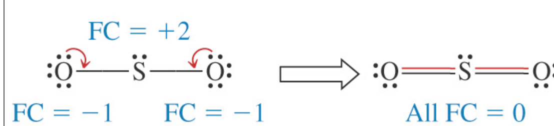
four bonds



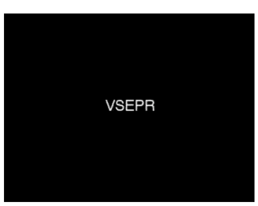
Formal Charge

- Equals the number of valence electrons of the free atom minus [the number of unshared valence electrons in the molecule + 1/2 the number of shared valence electrons in the molecule].
- Moving/Adding/Subtracting atoms and electrons.
- See examples on the board.

Formal charge = number of valence electrons –
(number of lone pair electrons +1/2 number of bonding electrons)



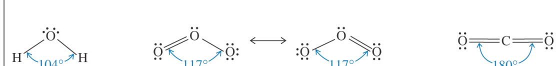
VSEPR Model
Valence Shell Electron Pair Repulsion



VSEPR Model

The molecular structure of a given atom is determined principally by minimizing electron pair (bonded &free) repulsions through maximizing separations.

Some examples of minimizing interactions.



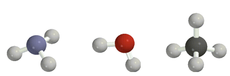
Predicting a VSEPR Structure

- 1. Draw Lewis structure.
- 2. Put pairs as far apart as possible.
- 3. Determine positions of atoms from the way electron pairs are shared.
- 4. Determine the name of molecular structure from positions of the atoms.

	Orbital Geometry	Molecular Geometry	Bond Angle	# of lone pairs
	Linear	Linear	180°	0
	Trigonal Planar	Trigonal Planar	120°	0
	Trigonal Planar	Bent	<120°	1
Chem 226	Tetrahedral	Tetrahedral	109.5°	0
	Tetrahedral	Trigonal Pyramidal	<109.5°	1
	Tetrahedral	Bent	<109.5°	2
	Trigonal Bipyramidal	Trigonal Bipyramidal	120°, 90°	0
	Trigonal Bipyramidal	Seesaw	<120°, <90°	1
	Trigonal Bipyramidal	T-shape	<90°	2
	Trigonal Bipyramidal	Linear	180°	3
	Octahedral	Octahedral	90°	0
	Octahedral	Square Pyramidal	<90°	1
	Octahedral	Square Planar	90°	2

Lewis Structures / VSEPR / Molecular Models

- Computer Generated Models



Ball and stick models of ammonia, water and methane. For many others see:
http://ep.llnl.gov/msds/pdb/
http://ep.llnl.gov/msds/orgchem/Chem226/Smell-Stereochem.html

Covalent Compounds

•Equal sharing of electrons: nonpolar covalent bond, same electronegativity (e.g., H_2)
• Unequal sharing of electrons between atoms of different electronegativities: polar covalent bond (e.g., HF)

TABLE 1.3 The Electronegativities of Selected Elements[a]

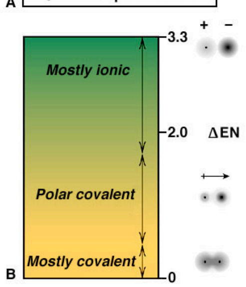
IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

increasing electronegativity → ; increasing electronegativity ↑

[a]Electronegativity values are relative, not absolute. As a result, there are several scales of electronegativities. The electronegativities listed here are from the scale devised by Linus Pauling.

Boundary Ranges for Classifying Ionic Character of Chemical Bonds

ΔEN	IONIC CHARACTER
>1.7	Mostly ionic
0.4-1.7	Polar covalent
<0.4	Mostly covalent
0	Nonpolar covalent



Drag any two elements to the designated boxes, and click "Calculate" to see where the bond falls on the continuum of bond types. Click "Start Over" to try another combination.

H						
Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K						Br
						I

Drag element here — Drag element here

Calculate

Start Over

ionic bond — polar covalent bond — nonpolar covalent bond

Bond Dipole & Dipole Moment

- Dipole moments are experimentally measured.
  - Polar bonds have dipole moments.

dipole moment (D) = □ = *e* x *d*

(*e*) : magnitude of the charge on the atom

(*d*) : distance between the two charges

Table 1.4 The Dipole Moments of Some Commonly Encountered Bonds

Bond	Dipole moment (D)	Bond	Dipole moment (D)
H—C	0.4	C—C	0
H—N	1.3	C—N	0.2
H—O	1.5	C—O	0.7
H—F	1.7	C—F	1.6
H—Cl	1.1	C—Cl	1.5
H—Br	0.8	C—Br	1.4
H—I	0.4	C—I	1.2

Bond Polarity

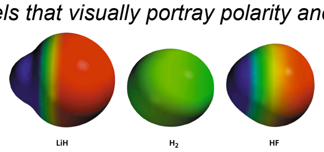
A molecule, such as HF, that has a center of positive charge and a center of negative charge is polar, and has a dipole moment. The partial charge is represented by □ and the polarity with a vector arrow.

H—F

□+ □□

Electrostatic Potential Maps

Models that visually portray polarity and dipoles



red < orange < yellow < green < blue

most negative electrostatic potential … **most positive electrostatic potential**

Hydrogen Halides

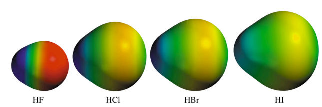
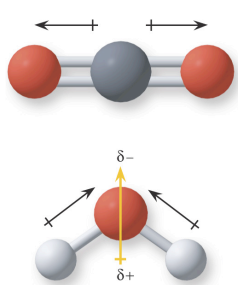


Table 1.6 Hydrogen–Halogen Bond Lengths and Bond Strengths

Hydrogen halide	Bond length (Å)	Bond strength kcal/mol	Bond strength kJ/mol
H—F	0.917	136	571
H—Cl	1.2746	103	432
H—Br	1.4145	87	366
H—I	1.6090	71	298

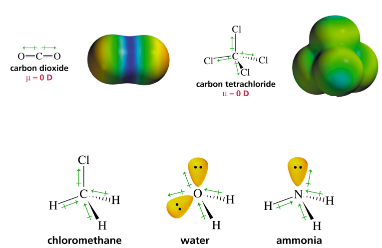
Molecular Polarity & Dipole Moment



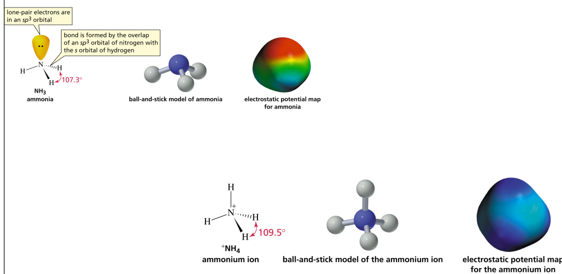
When identical polar bonds point in opposite directions, the effects of their polarities cancel, giving no net dipole moment. When they do not point in opposite directions, there is a net effect and a net molecular dipole moment, designated □

Molecular Dipole Moment

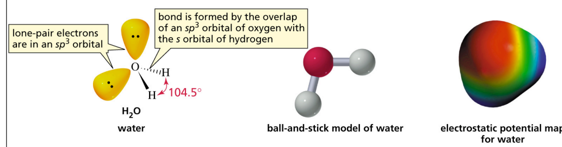
The vector sum of the magnitude and the direction of the individual bond dipole determines the overall dipole moment of a molecule



Ammonia and in the Ammonium Ion

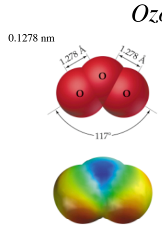


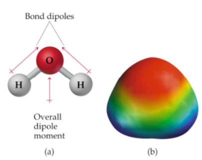
Water



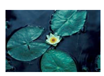
Polarity & Physical Properties

Ozone and Water





- Resultant Molecular Dipoles > 0
- Solubility: Polar molecules that dissolve or are dissolved in like molecules

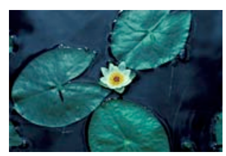


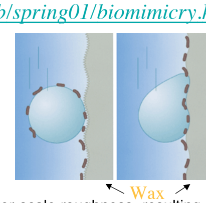
- The Lotus flower
- Water & dirt repellancy

The "Lotus Effect"

Biomimicry

http://www.bfi.org/Trimtab/spring01/biomimicry.htm



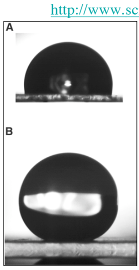


- Lotus petals have micrometer-scale roughness, resulting in water contact angles up to 170°
- See the Left image in the illustration on the right.

The "Lotus Effect"

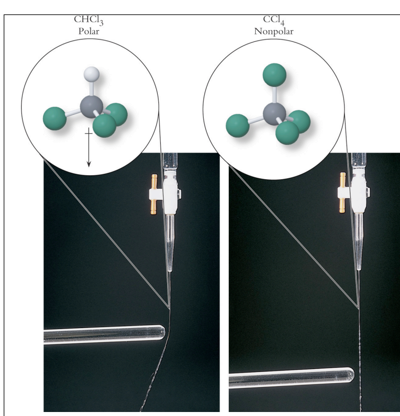
Biomimicry

http://www.sciencemag.org/cgi/content/full/299/5611/1377/DC1



- Isotactic polypropylene (i-PP) melted between two glass slides and subsequent crystallization provided a smooth surface. Atomic force microscopy tests indicated that the surface had root mean square (rms) roughness of 10 nm.
- A) The water drop on the resulting surface had a contact angle of 104° ± 2
- B) the water drop on a superhydrophobic i-PP coating surface has a contact angle of 160°.

Science, 299, (2003), pp. 1377-1380, H. Yldrm Erbil, A. Levent Demirel, Yonca Avc, Olcay Mert



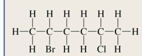
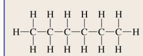
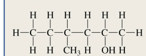
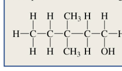
An electrically charged rod attracts a stream of chloroform but has no effect on a stream of carbon tetrachloride.

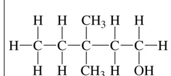
Molecular Representations

Representing Substances

Empirical Formula, Molecular Formula, Structure:
(Lewis, Kekule, ***Condensed, Line****),* ***Visual Model****:*
wireframe, stick, ball & stick, space filling, electrostatic, energy surface

Table 1.5 Kekulé and Condensed Structures

Kekul structur e	Condensed structures
Atoms bonded to a carbon are shown to the right of the carbon. Atoms other than H can be shown hanging from the carbon.	
	$CH_3CHBrCH_2CH_2CHClCH_3$ or $CH_3\underset{Br}{CH}CH_2CH_2\underset{Cl}{CH}CH_3$
Repeating CH_2 groups can be shown in parentheses.	
	$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$
Groups bonded to a carbon can be shown (in parentheses) to the right of the carbon, or hanging from the carbon.	
	$CH_3CH_2CH(CH_3)CH_2CH(OH)CH_3$ or $CH_3CH_2\underset{CH_3}{CH}CH_2\underset{OH}{CH}CH_3$
Groups bonded to the far-right carbon are not put in parentheses.	
	$CH_3CH_2C(CH_3)_2CH_2CH_2OH$ or $CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2OH$



$CH_3CH_2C(CH_3)_2CH_2CH_2OH$ or $CH_3CH_2\overset{CH_3}{\underset{CH_3}{C}}CH_2CH_2OH$

$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_3$ or $CH_3CH_2COCH_3$ or $CH_3CH_2C(=O)CH_3$

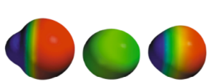
$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}H$ or $CH_3CH_2CH_2CHO$ or $CH_3CH_2CH_2CH=O$

$CH_3CH_2\overset{O}{\overset{\|}{C}}OH$ or $CH_3CH_2CO_2H$ or CH_3CH_2COOH

$CH_3CH_2\overset{O}{\overset{\|}{C}}OCH_3$ or $CH_3CH_2CO_2CH_3$ or $CH_3CH_2COOCH_3$

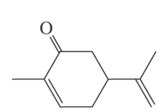
Molecular Representations

Empirical Formula, Molecular Formula, Structure:
(Lewis, Kekule, ***Condensed, Line****),* ***Visual Model****:*
wireframe, stick, ball & stick, space filling, electrostatic, energy surface

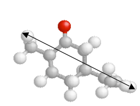


Worksheet: Organic Molecules I
http://ep.llnl.gov/msds/Chem120/226shapes-04.html

Line Drawing and Ball & Stick



Carvone
($C_{10}H_{14}O$)



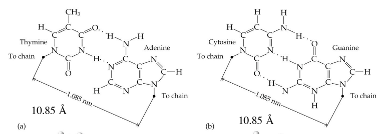
8.16 Å *(0.816 nm)*

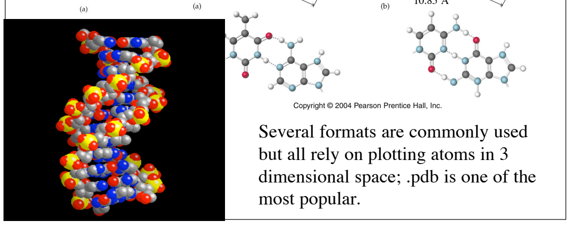
http://ep.llnl.gov/msds/orgchem/Chem226/Smell-Stereochem.html

Very Large Molecules:DNA

http://www.umass.edu/microbio/chime/beta/pe_alpha/atlas/atlas.htm

Views & Algorithms





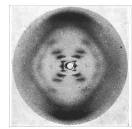
Several formats are commonly used but all rely on plotting atoms in 3 dimensional space; .pdb is one of the most popular.

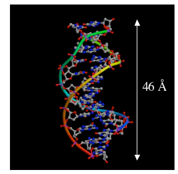
Very Large Molecules

http://info.bio.cmu.edu/courses/03231/ProtStruc/ProtStruc.htm

B-DNA: Size, Shape & Self Assembly

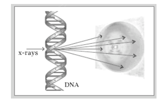
Rosalind Franklin's Photo





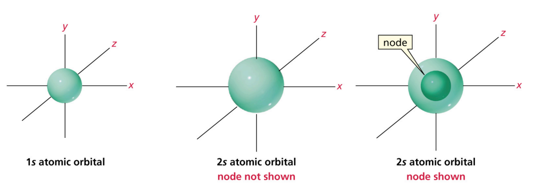
12 base sequence

(1953-2003)

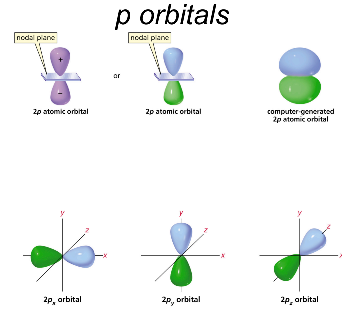


http://molvis.sdsc.edu/pdb/dna_b_form.pdb

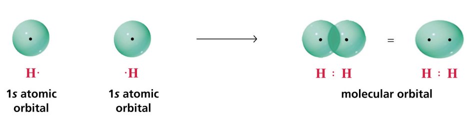
Atomic Orbitals
s orbitals



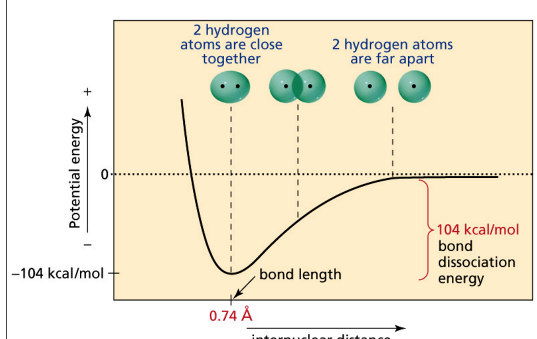
Atomic Orbitals
p orbitals



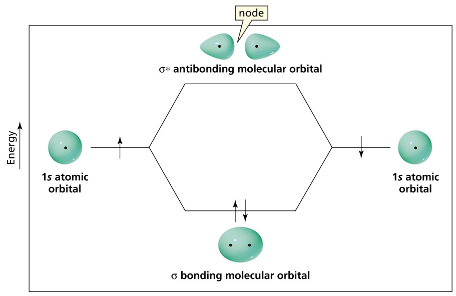
Molecular Orbitals



- Atomic orbitals mix to form molecular orbitals
- σ bond: formed by overlapping of two *s* orbitals

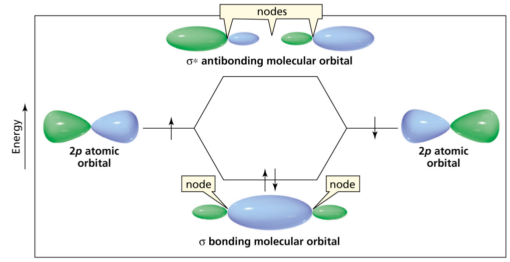


In-phase overlap of s atomic orbitals form a **bonding MO**; out-of-phase overlap forms an **antibonding MO**



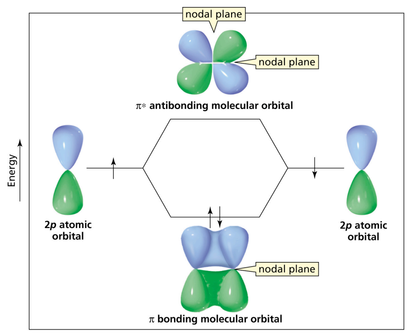
A single bond is a □ bond.

A sigma bond (□) is formed by end-on overlap of two *p* orbitals



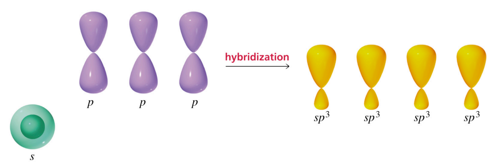
A □ bond is weaker than a □ bond.
Double bonds have 1 □ and 1 □ bond.
A double bond is shorter and stronger than a single bond.

Pi bond (□) is formed by sideways overlap of two parallel *p* orbitals

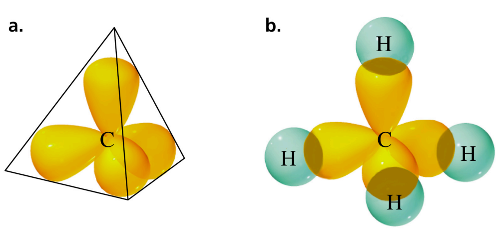


Bonding in Methane and Ethane: Single Bonds

Hybridization of orbitals:

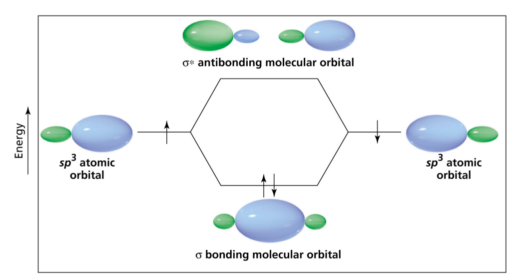


The orbitals used in bond formation determine the bond angles

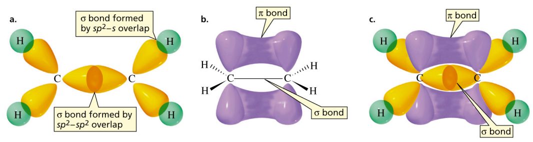


- Tetrahedral bond angle: 109.5˚
- Electron pairs spread themselves into space as far from each other as possible

Hybrid Orbitals of Ethane

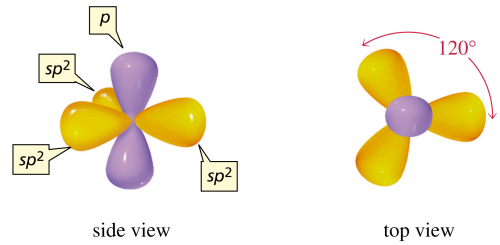


Bonding in Ethene: A Double Bond



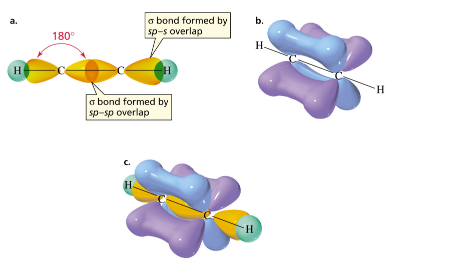
Double bonds have 1 □ and 1 □ bond.
A double bond is shorter and stronger than a single bond.

An *sp*-Hybridized Carbon

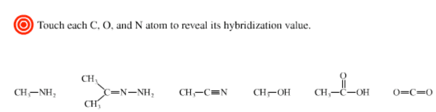


- The bond angle in the sp^2 carbon is 120˚
- The sp^2 carbon is the trigonal planar carbon

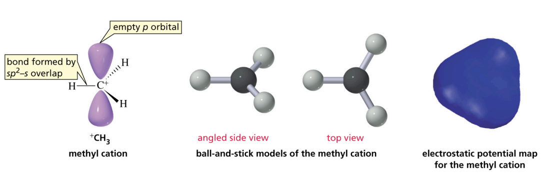
Bonding in Ethyne: A Triple Bond



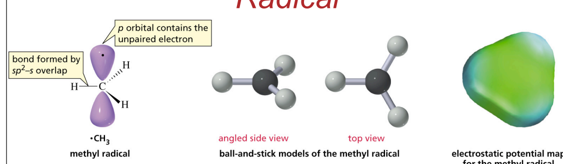
- A triple bond consists of one □ bond and two □ bonds
- Triple bonds are shorter and stronger than double bonds
- There is a bond angle of the *sp* carbon: 180˚



Reactive Intermediates
Carbocation

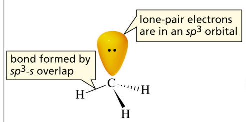


Reactive Intermediates
Radical

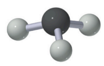


Reactive Intermediates

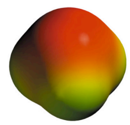
Carbanion



$\bar{:}CH_3$
methyl anion



ball-and-stick model of the methyl anion



electrostatic potential map for the methyl anion

Summary

- A □ bond is weaker than a □ bond
- The greater the electron density in the region of orbital overlap, the stronger is the bond
- The more *s* character, the shorter and stronger is the bond
- The more *s* character, the larger is the bond angle